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Comparison of methane hydrate formation in stirred reactor and porous media in the presence of SDS

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Abstract

In this work, methane hydrate formation was compared between a stirred reactor and a fixed bed of porous media (silica sand) in the presence of sodium dodecyl sulfate (SDS). The experiments were carried out in batch operation and at 7.0 MPa and 274.15 K. The aqueous concentration of SDS used was in the range of (300-1500 ppm). The results indicated that the SDS concentration of 500 ppm was found to be an optimum concentration for methane hydrate formation, and methane hydrate formation was significantly promoted in the fixed bed of silica sand with 500 ppm SDS as compared to those using SDS solutions in the stirred reactor. The water conversion to hydrate and the gas storage capacity achieved 78.1% and 139.8 V/V, respectively.

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Keywords: Gas hydrates; SDS; Porous media; Gas storage; Methane

1. Introduction

Gas hydrates are non-stoichiometric crystalline compounds in which small-sized guest molecules like CH_4, C_2H_6, CO_2 are trapped in host cages that are composed of hydrogen-bonded water molecules. Studies have been extensively conducted because gas hydrates are regarded as a sort of potential energy resource and a new approach for gas separation, natural gas storage and transportation, and CO_2 capture [1]. Rapid hydrate formation rate and high water conversion to hydrate are two significant factors for gas storage and transportation in the form of gas hydrates. Porous media are promising candidate to improve the kinetics of hydrate formation because larger contact area between the liquid water and the hydrate formers is created and the mixing of reactor contents is not needed as compared to the stirred reactor. Therefore, the energy cost will be greatly saved if this arrangement is scaled up for hydrate formation [2]. To better understand the kinetics of methane hydrate formation and improve the hydrate-based process

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for natural gas storage, methane hydrate formation in a stirred reactor and in a fixed bed of porous media (silica sand) is compared in the present work. The anionic surfactant sodium dodecyl sulfate (SDS) is employed to enhance the rate of methane hydrate formation, and the influences of porous media and the concentration of SDS on methane hydrate formation are discussed as well.

2. Experimental Section

2.1 Materials

Methane gas with a certified purity of 99.99% was supplied by Chongqing Rising Gas. Sodium dodecyl sulfate (SDS) with a mass purity of 99% was purchased from Chongqing Oriental Chemical Co., Ltd. Silica sands were purchased from Nanjing Chemical Reagent Co. Ltd. Deionized water was used in all experimental runs. The surface area of the pores is 0.17 m^2/g and the average pore diameter is 59.5 nm, which were measured using the surface area and porosity analyzer (Micromaritics ASAP 2010, USA). The SEM images of silica sands were captured using Phenom ProX SEM (FEI company).

2.2 Apparatus and procedure for hydrate formation

Detailed description of the apparatus (600 cm^3) and formation procedures was given in our early paper [3]. A 140 cm^3 SDS solution was used in the stirred reactor. The experiments using the fixed bed of silica sand were performed in the same reactor with the removal of the stirrer. Then a mass of 270 g silica sands was charged in the vessel at a height of 4.8 cm and saturated by 70 cm^3 SDS solution. Two parallel experiments were conducted under each condition. The gas uptake (Δn_H, mol), rate of hydrate formation (RHF), water conversion to hydrate, and storage capacity (gas volume per unit volume of gas hydrate, V/V) were determined by the equations presented in the literature [4,5]. The normalized gas uptake ($\Delta n_H/n_W$, mol of gas /mol of water) was obtained by dividing the moles of water (n_w) into the gas uptake.

3. Results and Discussion

Table 1 shows the experimental conditions along with the measured induction times (t_{ind}), normalized gas uptake, water conversion to hydrate, and storage capacity obtained in the stirred reactor (experiments 1-8) and in the fixed bed of silica sands (experiments 9-12). The experiments were carried out in batch mode and at 7.0 MPa and 274.15 K. As seen, the results of the stirred reactor indicate that 500 ppm SDS was the best concentration for methane hydrate formation among all the SDS concentrations (300, 500, 1000, and 1500 ppm) used in this work. This result is in good agreement with what was reported in the literature [5].

Table 1. Summary of experimental conditions and results for methane hydrate formation at 7.0 MPa and 274.15 K

Exp. No	Experiment format	SDS (ppm)	t_{ind} (min)	RHF at 30 min (mol/h)	Normalized gas uptake (mol of gas/ mol of water)	Water conversion to hydrate (%)	Storage capacity (V/V)
1	Stirred reactor	300	6	1.2665	0.1259	72.4	130.6
2			5.6	1.1816	0.1254	72.1	130.0
3		500	2	1.4696	0.1356	77.9	140.6
4			1	1.2116	0.1333	76.6	138.2
5		1000	1	0.8754	0.0739	42.5	76.6
6			0.7	0.9923	0.0834	48.0	86.5
7		1500	1	1.1629	0.0963	55.4	99.8
8			1	1.0814	0.0859	49.4	89.1
9	Silica sand	500	0.2	0.7652	0.1363	78.4	140.3
10			0.8	0.7796	0.1354	77.8	139.3
11	Silica sand	0	28.2	0.1120	0.1078	62.0	111.0
12			63	0.0736	0.0962	55.3	99.0

Fig. 1 shows the temperature and gas uptake curves for the experiment performed at 7.0 MPa, 274.15 K, and 500 ppm SDS in the stirred reactor. The induction time was determined at 2 min by a sudden temperature rise in the liquid phase, indicating that methane hydrate nucleation occurred immediately when the experiment was started in the presence of SDS. This is attributed to the significant reduction of the aqueous surface tensions with the addition of SDS to the liquid phase. The gas uptake was also observed to increase rapidly at the nucleation point. Then the gas uptake increased slowly and achieved a plateau at the end of the experiment. This trend of the gas uptake curve is probably due to the progressive accumulation of methane hydrate at the gas/liquid interface and hence the mass transfer of methane gas to the reaction interface is blocked.

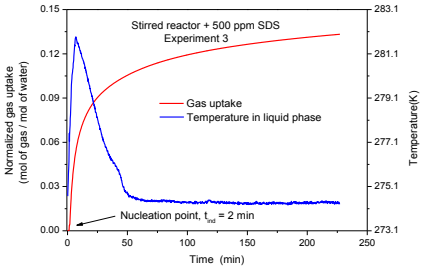

Fig. 1. Temperature and gas uptake curves for methane hydrate formation in stirred reactor at 500 ppm SDS.

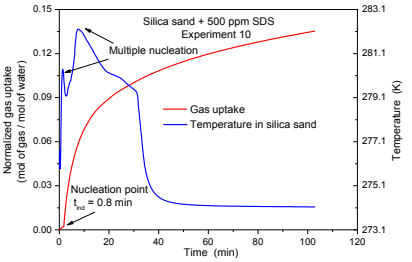

Fig. 2. Temperature and gas uptake curves for methane hydrate formation in fixed bed of silica sand at 500 ppm SDS

Experiments were also carried out with 500 ppm SDS in a fixed bed of silica sands for comparison. Fig. 2 shows that methane hydrate quickly nucleated at 0.8 min. This is much faster than that observed in the stirred reactor. Interestingly, multiple temperature peaks were observed in the silica sand bed, indicating that hydrate formation occurred in different positions of the sands bed. This probably results in a more amount of methane hydrate formed. As seen in Table 1, the gas consumption obtained in the fixed bed of silica sand at the same SDS concentration (experiment 9-10) was higher as compared to those obtained in the stirred reactor (experiments 3-4). The storage capacity was also increased in the silica sand bed.

Fig. 3 shows the SEM images of silica sands. It can be clearly seen that the shape of sand particles is irregular and hence a large number of nucleation sites are available for hydrate formation. Also, interstitial spaces between sand particles and the micro pores on the sand particles can be seen in the figure. This leads to a significant increase of the contact area between methane gas and liquid phase as compared to the gas/liquid interface in the stirred reactor. This might be the proper reason for the enhancement of methane hydrate formation that was observed in the fixed bed of silica sands.

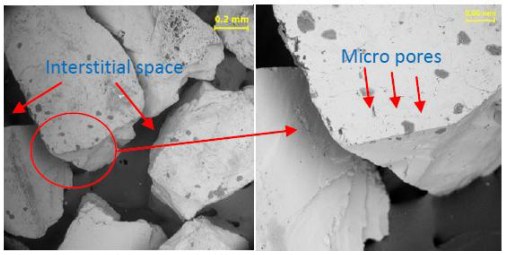

Fig. 3. SEM images of silica sands

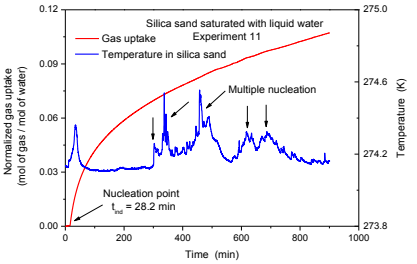

Fig. 4. Temperature and gas uptake curves for methane hydrate formation in the fixed bed of silica sand without SDS

Fig. 4 shows the temperature and gas uptake curves for the experiment conducted in the fixed bed of silica sands in the absence of SDS. The induction time was determined at 28.2 min by a sudden temperature increase in the silica sand bed, which is longer than that obtained in the presence of SDS

(experiments 9-10). This comparison indicates that the presence of SDS promoted methane hydrate nucleation in the fixed bed of silica sand. Multiple temperature peaks were also observed in the absence of SDS. This is evidence of multiple hydrate formation event occurred in the fixed bed of silica sands. However, the intensity of temperature spikes is weaker than that observed in the presence of SDS (Fig. 2). This result indicates that more amount of methane hydrate was formed in the presence of SDS and more hydration heat was released accordingly. This is also confirmed by the results reported in Table 1. As seen, the average gas uptake obtained in the presence of SDS is 0.1359 mol of gas /mol of water, while that obtained in the absence of SDS is reduced to 0.102 mol of gas /mol of water.

Fig. 5 shows the comparison of storage capacity obtained at different SDS concentrations. The storage capacity obtained at 500 ppm SDS is higher than those obtained at other SDS concentrations. Interestingly, the storage capacity obtained at 500 ppm SDS (~139.8 V/V) in the silica sand is almost the same as that obtained at the same SDS concentration (~139.4 V/V) in the stirred reactor. This indicates that the silica sand saturated with 500 ppm SDS solution can be used for the promotion of CH_4 hydrate formation instead of the stirred reactor. However, compared to the theoretical value (~180 V/V), there is still a space to increase the storage capacity in the fixed bed of silica sand before widely used in industries.

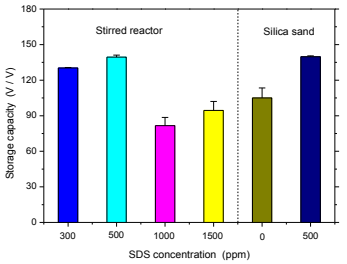

Fig. 5. Comparison of storage capacity in the stirred reactor and in the fixed bed of silica sands

4. Conclusions

In this work, methane hydrate formation was compared between a stirred reactor and a fixed bed of silica sands in the presence of SDS. The 500 ppm SDS is an optimum concentration for methane hydrate formation. Methane hydrate formed at 500 ppm SDS in silica sands was significantly promoted compared to that in the stirred reactor and in the absence of SDS. The gas uptake obtained was as high as 0.1359 mol of gas / mol of water and the corresponding storage capacity was approximately 139.8 V/V.

Acknowledgements

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